

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for review of data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports (4302). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not have a valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

AFRL-SR-BL-TR-01-

aining the
reducing
22202-
a currency

0533

1. REPORT DATE (DD-MM-YYYY) 9/24/01		2. REPORT TYPE Final		3. DATES COVERED (From - To) 12/01/99 - 10/31/00	
4. TITLE AND SUBTITLE Lithium Intercalation of Carbon-Nanotube Electrodes				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER F49620-00-1-0203	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) David T. Shaw				5d. PROJECT NUMBER 2303 - BV	
				5e. TASK NUMBER 61102F	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Research Foundation of SUNY State University of New York at Buffalo 520 Lee Entrance, Suite 211 Amherst, NY 14228				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAF Office of Scientific Research Building 410 Bolling AFB Washington, DC 20332-6448				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) F496200010203	
12. DISTRIBUTION / AVAILABILITY STATEMENT AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR) NOTICE OF TRANSMITTAL DTIC. THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLIC RELEASE LAW AFR 190-12. DISTRIBUTION IS UNLIMITED.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT High aligned multiwall nanotubes (MCNTs) have been obtained by catalytic decomposition of carbon-containing organic compounds by plasma-enhanced hot-filament chemical vapor deposition (PEHFCVD) on nickel substrates. Such a MCNT-based structure serves as a convenient material for studying the electrode process of lithium-ion intercalation. Lithium insertion electrochemical measurements were performed and charge/discharge capacities were determined. Results showed the MCNT arrays inserted and de-inserted lithium with considerable irreversible capacities. This may have resulted from the formation of acetone/alcohol insoluble films on MCNT arrays. Future studies should concentrate on the effects of MCNT-array conditions (e.g., opened or closed ends, nanotube size, length and density) on the intercalation irreversibilities.					
15. SUBJECT TERMS					
20011026 008					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

OVERVIEW OF WORK ACCOMPLISHED

Multiwall carbon nanotubes were used to study the electrode process of lithium ion intercalation. Lithium insertion electrochemical measurements were performed and charge/discharge capacities were determined. Results shared:

- The discharge capacity of the electrode decreases with increasing discharge rate, indicating concentration polarization effects at higher discharge rates.
- The charge capacity of the electrode decreases with increasing discharge number. This is attributed to the decreased amounts of lithium extracted during experiments at higher discharge rates.

As this study indicates, MCNT arrays insert and de-insert lithium with considerable irreversible capacities. The effect of MCNT array conditions on the intercalation irreversibilities is an important area for future study.

INTRODUCTION

Multiwall carbon nanotubes (MCNTs) consist of graphene sheets stacked in an organized manner. If they are organized coaxially, MCNTs are modeled like "Russian dolls" with the concentric cylinders stacked together. The number of graphene sheets ranges from two to a few hundred, and MCNT diameters are in the range of 5 to 150 nm. The length is controlled by the growth time, typically in the range of 10-30 microns. For concentric MCNTs, both ends are typically closed (or capped) by graphene layers, and the number of layers are the same as the side walls. The MCNT caps can be easily removed (e.g., by oxidation).

Theoretically, for closed concentric MCNTs, lithium insertion can only take place outside the MCNTs. If MCNTs are opened, lithium ions, which have an ion radius of 0.72 Angstroms, can be inserted either in the inside core (diameter ~1.2 Angstroms) or between graphene sheets (distance ~3.45 Angstroms). In fact, most MCNTs are not concentric. For example, our MCNT arrays grown by PEHFCVD techniques are made up of v-shaped longitudinal graphene sheets. Instead of "Russian doll" concentric cylinders, the MCNTs are patterned after a stack of cones with graphene sheets opened on the MCNT sidewalls. Matsumura suggested that for such "open" MCNTs, Li ions are not only intercalated between graphene layers, but also doped at the edge of the graphene layers, as well as at the core and outside walls.

EXPERIMENTAL SET UP AND PROCEDURE

Samples were prepared by plasma-enhanced hot-filament chemical vapor deposition technique. Detailed procedures have been described elsewhere. Briefly, the plasma-enhanced HFCVD system is comprised of a Ta electrode installed above a 0.3 mm diameter tungsten hot filament, which is used to dissociate the inlet gas mixtures ($N_2/H_2/CH_4$). An initial blast of plasma current is needed to generate nanometer-size

particles from the metallic substrate. These particles act as catalyst for CVD growth of aligned MCNTs. By controlling the processing parameters (plasma conditions, gas-mixture composition and pressure, filament and substrate temperatures), the MCNTs diameter, density, and length can be reproducibly controlled. The adhesion between the MCNTs and the metallic substrate is very strong. The current collectors fabricated by HFCVD directly on metallic substrates appeared to be ideally suited for the electrochemical experimental testing described below. In order to understand the mechanisms of lithium-ion intercalation and diffusion, as well as the effects of surface film formation, electrodes with MCNTs aligned (1) perpendicular, (2) parallel, and (3) 45° to the substrates were used. These direction-dependent samples were prepared by controlling the E-field direction during the MCNT growth.

The mass of CNTs deposited on Ni substrates was typically approximately 1 mg/cm². Typical sizes of the deposited samples were 2.5 cm². The samples were cut into small pieces, each with an area of about 0.5 cm².

Li-insertion electrochemistry was performed in an argon-filled glove bag. Lithium counter and reference electrodes were used, and the electrolyte was 1 M LiClO₄ in a 7:3 (v/v) mixture of diethyl carbonate and ethylene carbonate. Prior to use, the solvent blend was dried over a molecular sieve to remove water. An EG&G 273A controlled with EG&G M270 software was used for the electrochemical measurements. Charge experiments were performed to a voltage cutoff (VC) of 5 mV vs. the lithium reference electrode.

DISCUSSION OF RESULTS

Figure 1 shows the results of the first charge (lithium insertion) and discharge (lithium extraction) experiments performed at 10 and 25 μA respectively. The graph shows that the first charge capacity of the carbon nanotube array was approximately 427 mAh g⁻¹. This is higher than the theoretical capacity of 372 mAh g⁻¹ for graphite (ref). The first discharge capacity was 277 mAh g⁻¹. Assuming a maximum capacity of 372 mAh g⁻¹ for this electrode, the charge and discharge rates were 16.7 °C and 6.7 °C respectively.

The capacity of both charge experiments was higher than that for the discharge experiment. This could be due to the different rates used. Note also that the capacity of the second charge (391 mAh g⁻¹) was significantly higher than the capacity of the first discharge. This probably indicates that there was some irreversible capacity during charging to 5 mV relative to the lithium reference.

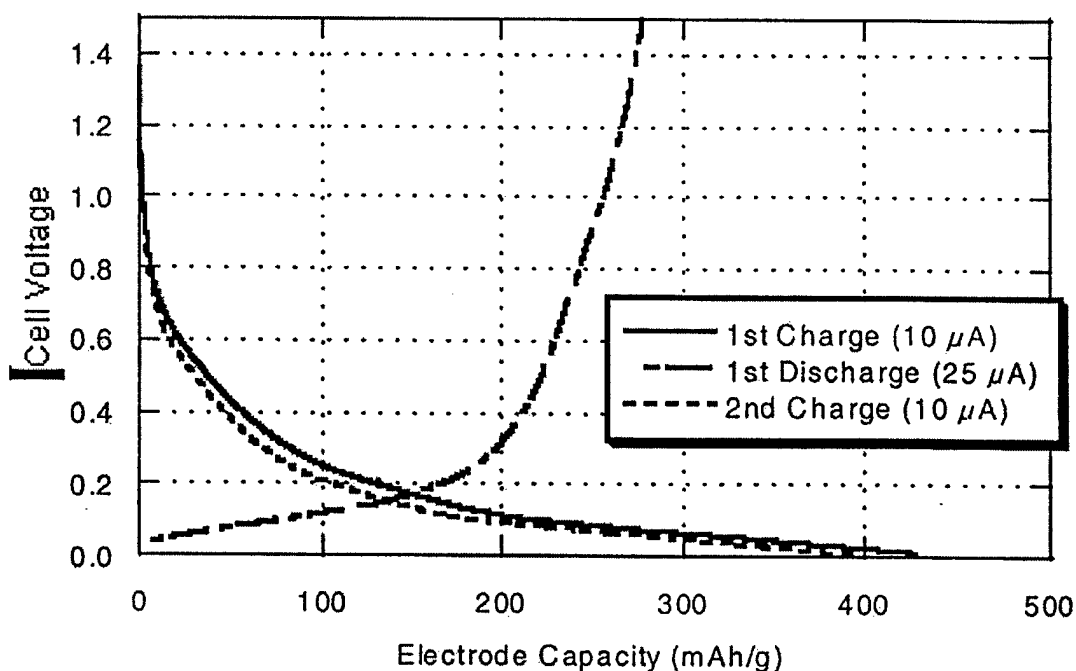


Figure 1. First and second charge and first discharge experiments for specimen N₄.

To explore the rate capacity of the electrode, a series of experiments were performed at various discharge rates. To begin, the electrode was charged at 10 μA to a VC of 5 mV. The electrode was then equilibrated at 5 mV for 30 minutes in order to obtain full charge capacity. After this equilibration, the electrode was discharged to a VC of 1.5 V. This protocol of charge/equilibration/discharge was repeated for various discharge rates. Table 1 shows the results of these experiments.

Table 1. Charge and discharge capacities of the carbon nanotube array.

Charge Number	Charge Capacity (mAh g ⁻¹)	Discharge #	Discharge Rate C rate (μA)	Discharge Capacity (mAh g ⁻¹)
1	372	1	C/7 (25)	272
2	326	2	C/3 (50)	261
3	302	3	C (150)	233
4	267	4	3C (500)	135

These data show that the discharge capacity of the electrode decreases with increasing discharge rate. This was likely due to concentration polarization effects at higher discharge rates. It should also be noted that the charge capacity of the electrode decreases with increasing discharge number. This was likely due to the decreased amounts of lithium that were extracted during experiments at higher discharge rates.

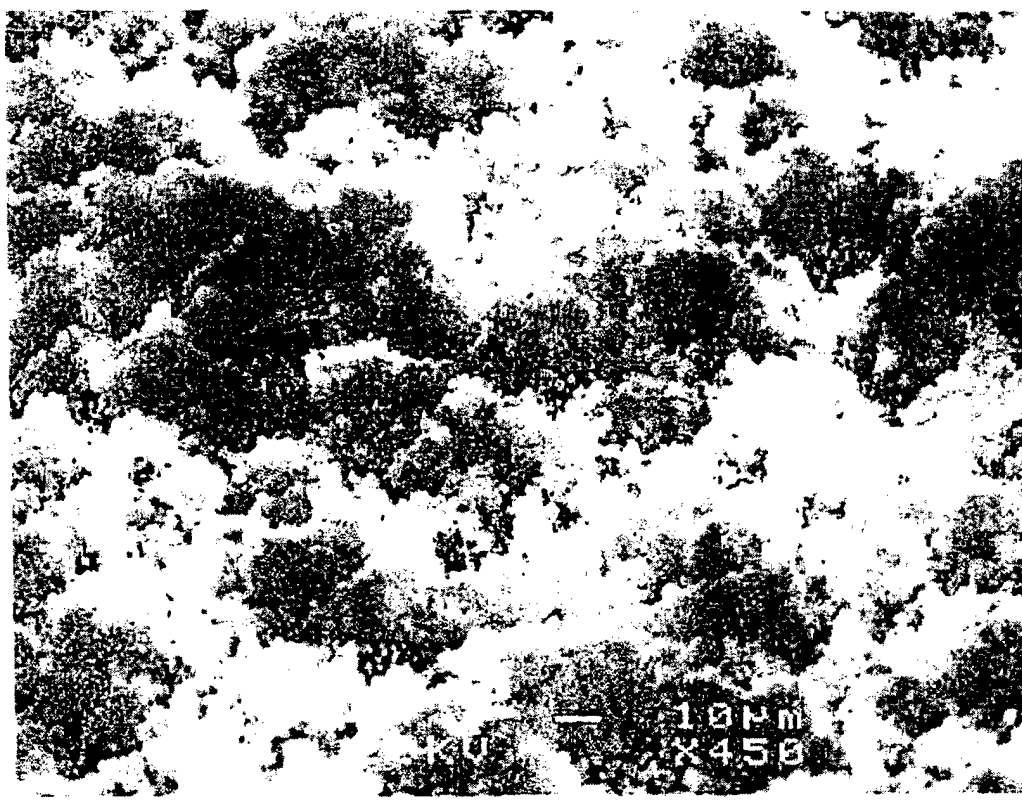


Figure 2. SEM picture of the insoluble film deposited on CNT electrode.

After the electrochemical experiments, SEM and EDS were performed to examine electrode morphology and elemental composition. The electrode was rinsed with acetone and isopropanol and dried under vacuum at room temperature prior to the analysis. After removal from the vacuum oven, the carbon nanotube array was white in color. This indicated that there was a coating on the carbon nanotubes that was formed during the electrochemical experiments. SEM analysis of this white area showed that it was a thick, rough film. Figure 2 is an SEM picture of this film. None of the carbon nanotubes were visible through the film. The wavy appearance of these tubes was the result of electronic noise during image acquisition. An EDS analysis of the film indicated the presence of carbon and oxygen. Thus, the film could contain lithium carbonate, which is typically deposited on the surface of carbon anodes during cycling in Li-ion battery experiments. Lithium carbonate results from decomposition of the carbonate-based electrolyte during charging experiments as the potential approaches that of the lithium reference.

INTERACTION

The project was carried out with the cooperation of Charles Patrissi of the Naval Undersea Warfare Center of Newport, Rhode Island.

PROJECT PERSONNEL

Partial support for two technicians, James Ye and Yan Chen, and a research post-doc, Xuedong Bai.

PUBLICATIONS

1. Y. Matsumura, et al., *Carbon*, 33, 1457 (95).
2. Y. Chen, S. Patel, Y. Ye, D. T. Shaw, *Appl. Phys. Lett.*, 73, 2119 (98).